HUMIDITY, PHOTO- AND GAS SENSITIVITY OF ZINC OXIDE THIN FILM TRANSISTOR

by
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Abstract

The humidity, photo- and NO2 sensing properties of the solution-processed ZnO thin film transistor (TFT) on a SiO2/Si substrate with Au electrode were investigated.

It is found that the device is highly sensitive and responds rapidly to these stimuli. 90.4%, 82.4% and 33.5% of sensitivity are achieved for humidity, photo and NO2 respectively characterized by the change of the source-drain current of the transfer curve after exposure. Possible sensing mechanisms are discussed for each stimulus. Besides, the device also exhibits high mobility and excellent stability under ambient conditions. These results indicate that ZnO thin film transistor is a promising sensor material.

Advisor: Howard E. Katz

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1. Introduction

Over the last few decades, with the arrival of the industrialization, air pollution has become a great issue threatening our environment. Moreover, flammable and explosive gases can cause great damage to life and property. So, real-time and effective detection of these gases is of vital importance. In addition to gas sensing, the humidity control and light detection are also essential for various fields of industry as well. For example, monitoring relative humidity in moisture-sensitive environments such as glove boxes and clean rooms are crucial for scientific research. UV detection is a very useful method in food inspection and flame detection as well as analytics such as spectroscopy.

Zinc oxide(ZnO) is a thoroughly studied post-transition-metal oxide which has many applications such as solar cells[1], photo detectors[2], gas sensor[3] and light emitting devices[4]. It is a wide band gap semiconductor material (3.4eV) exhibiting n-type characteristic and excellent chemical and thermal stability[5-7]. More recently, it is attracting considerable attention for its application in thin film transistors as the active channel material. The main advantage of using ZnO lies on its high mobility and easy preparation. The mobility reported in the literature ranges from 0.2 to 7 cm^2/Vs with an on/off ratio from 10^5 to 10^7 and a threshold voltage between -1 and 15V[8].

Intrinsic ZnO is sensitive to light[2], humidity[9] and different kinds of gases including O2[10-11], NH3[12], NO2[13], ethanol[14] etc. Its sensing property mainly comes from the point defects, especially oxygen vacancies, on ZnO surfaces which will produce very large changes in the surface conductivity. This change of conductivity is a result of charge transfer and band bending caused by the absorbates.

Several methods are used to prepare ZnO layers for thin films transistors including vacuum-based deposition such chemical vapor deposition[15] and magnetron sputtering[16] and solution-based deposition methods such as sol-gel process[17] and chemical bath deposition[18] etc. Vacuum deposition generally yields better transistor performance, especially higher mobility. For example, ZnO TFT fabricated by radiofrequency magnetron sputtering showed mobility above $30cm^2/Vs$[19]. However, vacuum deposition is very expensive and has high energy consumption due to vacuum deposition equipment. Among all techniques, the solution-processed method is most suitable for large area coating, low cost and low temperature processing. Moreover, solution-processed thin film semiconductors can potentially enable low-cost thin film transistor arrays via roll-to-roll process using a combination of conventional coating and printing techniques.

In this work, we use a simple solution process to prepare ZnO thin film followed by a thermal annealing of the film. The device was found to be stable under ambient conditions with superior TFT performance. We then studied the sensing properties of the device. High sensitivity, fast response and substantial recovery under humidity, photo- and NO_2 gas environment were demonstrated.

2. Experiment Section

2.1 Materials Preparation

The precursor solutions was prepared by dissolving zinc acetate dihydrate in 2-methoxyethanol(Sigma-Aldrich) stabilized by 2-ethanolamine(Sigma-Aldrich) with a 1:1 molar ratio with respect to the zinc acetate. The 2-ethanolamine acted as stabilizing agent for the formation of a stable solution. The solution was stirred under room temperature for 3 hours to completely dissolve the solute. By diluting with 2-methoxyethanol, precursor solutions with different concentration of 0.05M, 0.1M and 0.25M were prepared.

2.2 Device Fabrication

Silicon substrate coated with 200nm thick SiO_2 layer as dielectric layer was first immersed in piranha solution for 2 hours to remove the organics on the substrate followed by standard water-acetone-isopropanol ultrasonic cleaning. After cleaning, the substrate was dried by nitrogen gas and then subjected to UV-Ozone cleaning for 20min. The precursor solution of a specified concentration was spin-coated on top of the substrate at a spin speed of 1000rpm for 1min. The film was instantly preheated on a hot plate at 180°C for 10min and then annealed at 500°C in the furnace for 30min to convert the zinc acetate into ZnO. The above process was repeated 3 times with the concentration order of precursor solutions for each deposition being 0.05M, 0.1M and 0.25M) in order to obtain desired thickness. To complete the device fabrication, 50nm of gold was thermally evaporated through a shadow mask on top of the as-prepared

ZnO thin film as source and drain electrodes. The length(L) and width(W) of the channel are 40μm and 7000μm.

2.3 Characterization

The transistor characteristics were investigated by Keysight Agilent 4155C analyzer. The gas sensing properties were investigated by flow-through technique at atmospheric pressure using an Environics Gas Dilution Gas System (Series 4040). Meanwhile, the humidity sensitivity was investigated by adding 1.5ml of deionized water into the chamber of the probe station and the photosensitivity was investigated by controlling the level of the light intensity of the lamp.

3. Result and Discussion

Figure 1 shows typical FET properties of the device. The on/off ratio of the device is about 10^3 and the threshold voltage is 2.5V determined from the relationship between the square root of the transfer curve. The mobility in the linear regime($V_{DS}<V_{GS}$) is 2.4cm^2/Vs determined from[20-22]

$$I_{DS} = V_{DS} \times C_i \times \mu(V_{GS} - V_T)\frac{W}{L}$$

where I_{DS} is the source-drain current, V_{DS} is the source-drain voltage, C_i is the capacity of the SiO_2 dielectric layer, μ is the mobility, V_{GS} is the gate voltage, V_T is the threshold voltage, W is channel width and L is the channel length.

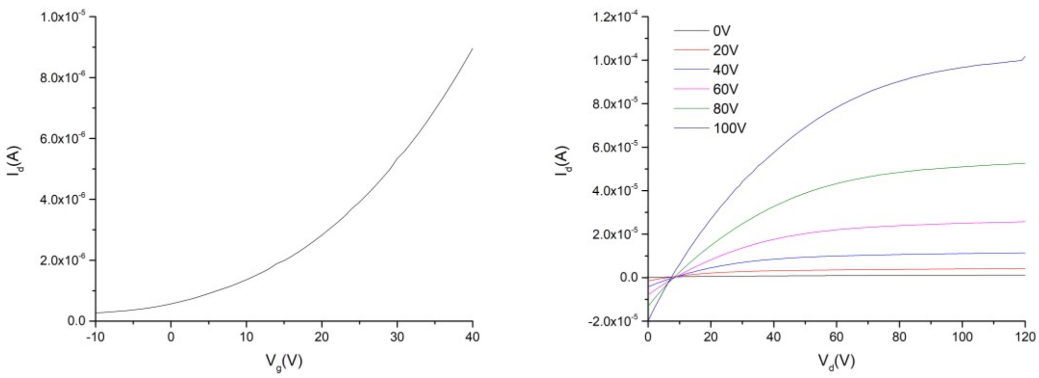

Figure 1: Transfer curve (left) and output curve (right) of the ZnO thin film transistor

The device is stable under ambient condition without taking precautionary measures to exclude ambient light, moisture and oxygen. As shown in Figure 2, after being placed in the drawer for 7 days, the drain current of the device dropped by 5% measured at V_g=40V. This drop mainly comes from the interaction of the device with the water in the air. The detailed mechanism will be discussed in the humidity sensitivity section below.

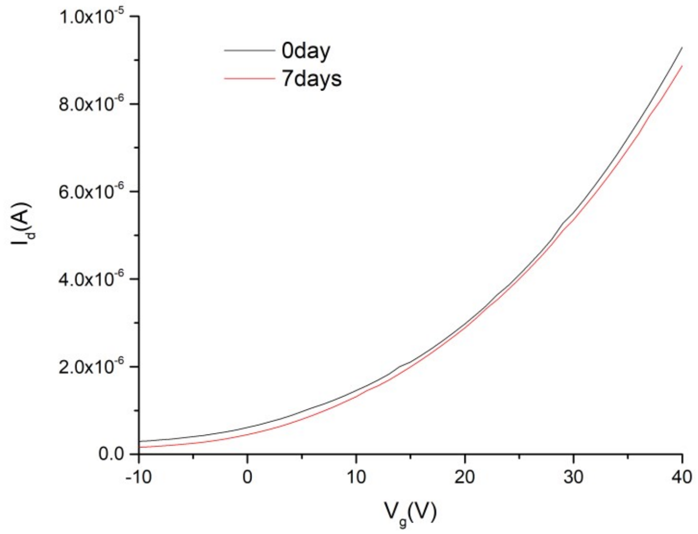

Figure 2: Transfer curve of the device tested immediately after device fabrication (black) and after being placed in the drawer for 7 days (red)

Figure 3 shows the change of transfer curve of the device after introducing the humidity source by placing 1.5ml of deionized water inside the sealed chamber of the probe station. All the transfer curves are tested under constant room light. As we can see from the transfer curve, the drain current drops immediately after introducing the humidity source for 30s and gradually becomes saturated after 210s. The response of the devices to humidity are shown by plotting drain current at V_g=40V versus exposure time (Figure 4). Sensitivity is defined in this work as

$$S = 100\% \times \frac{I'_{DS} - I_{DS}}{I_{DS}}$$

where I_{DS} is the initial drain current and I'_{DS} is the drain current after exposure. So, as shown in Figure 5, the sensitivity of the device to 15ml deionized water is 90.4%. The humidity-sensing mechanism of ZnO thin film transistor is mainly attributed to the reduction in carrier mobility. When the device is exposed to a humid environment, the water molecular will diffuse into grain boundary of the ZnO grains which will induce charge-dipole interactions with semiconductors. These interactions increase the energy barrier for charge-carrier transport and thus reduce the mobility of the devices. It is well known that response and recovery behavior is an extremely important characteristic for evaluating the performance of humidity sensor. So, after the device is saturated, we removed the humidity source, evacuated the moist air and refilled with dry air. It can be seen from Figure 3 (the second curve from top to bottom) that the device shows a 88.2% of recovery of the drain current.

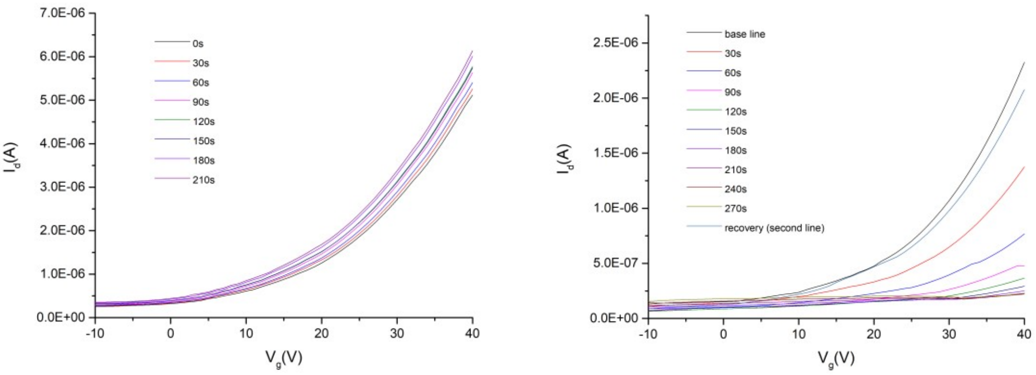

Figure 3: Transfer curves of the device tested every 30s under ambient condition (left) and under moisture air (right).

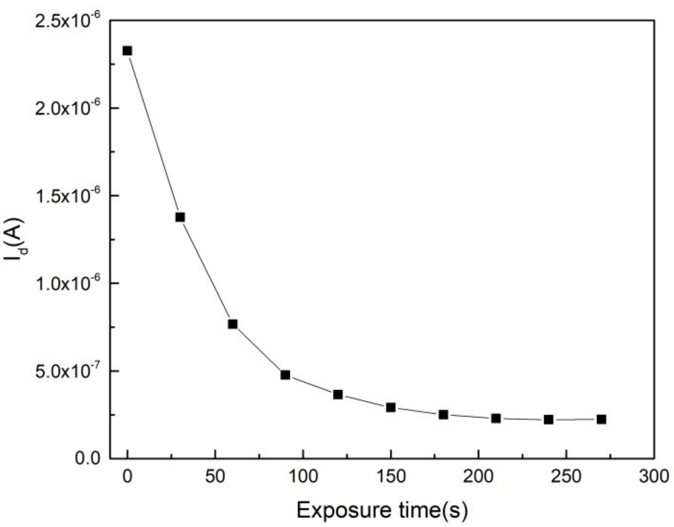

Figure 4: drain current of the device at V_g=40V versus exposure time

The photosensitivity of the device is also studied. As shown in Figure 5, the drain current will drop continuously in the dark while under light it will increase dramatically. The light intensity is controlled by changing the level of the lamp from level 1 to level 10 (lowest to highest). As we can see in Figure 6, the device shows 10% of sensitivity at very low light intensity and changes remarkably with different light intensities. The trend is almost linear at high intensity which means it is a promising material for photo detection. The mechanism of photosensitivity of ZnO is attributed to the photo-generated carriers which can be explained by band theory. The band gap of intrinsic ZnO is 3.4eV which gives an absorption wave length at 365nm or lower. Under illumination, the electrons on the valence band are excited to the conduction band as free excitons. Therefore, the conductivity of the ZnO will increase remarkably.

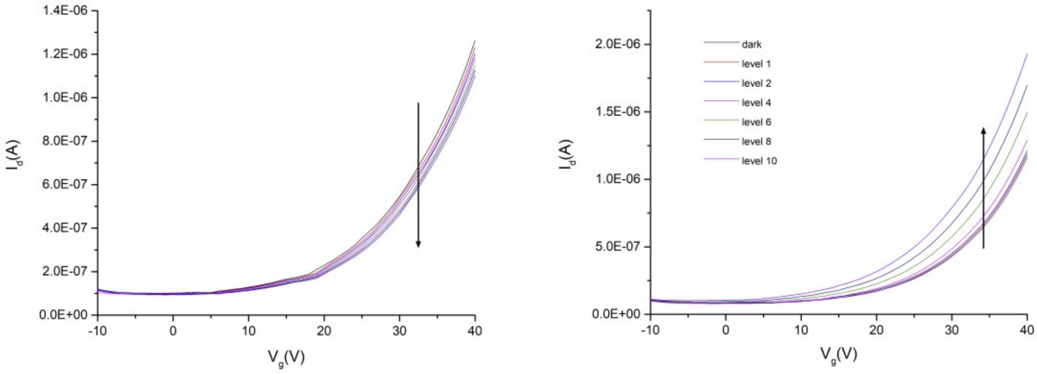

Figure 5: Transfer curves of the device tested every 10s in dark (left) and under increasing light intensity ranging from level 1 to level 10 (right)

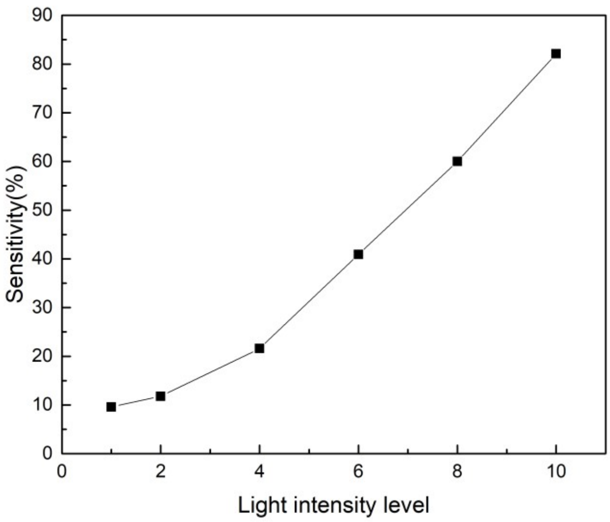

Figure 6: Photosensitivity of the device versus light intensity level

The response of the device to NO_2 gas is shown in Figure 7. After introducing NO_2 at 15min, the drain current dropped dramatically. The sensitivity is shown in Figure 8. As the concentration of NO_2 goes up, the sensitivity will increase at first and become saturated at high concentration. After that, the device will be less sensitive to the change of NO_2 concentration. The mechanism of the gas sensing properties of semiconductor materials was introduced by Weisz[23]. According to Weisz, when oxidizing gas, in our case, the NO_2 molecules, diffuse to the surface of the ZnO thin film, they will capture the electron in the film forming anion absorption. The accumulation of space charge around absorbates in the boundary layer of the film will act as a depletion region to increase the surface potential barrier. This potential barrier will cause band bending, thus impeding the motion of electrons. Therefore, the absorption of oxidizing gas will lower the current of semiconductor materials.

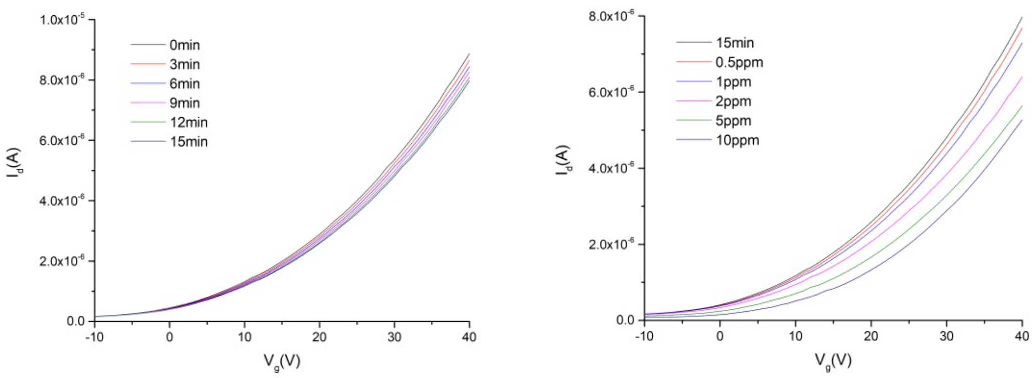

Figure 7: Transfer curves of the device tested every 3min in clean air (left) and in different concentration of NO_2 (right)

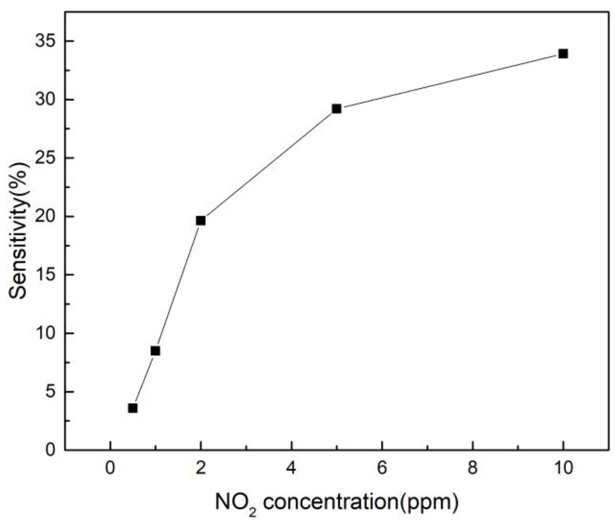

Figure 8: Sensitivity of the device to NO_2 versus NO_2 concentration

4. Conclusion

We have prepared ZnO thin film transistor through solution process with high mobility and excellent stability. The sensing characteristics to humidity, photo and NO_2 gas are carefully studied. In responses to humidity, 90.4% of sensitivity and 88.2% of recovery was achieved. In addition to humidity sensitivity, the device also shows high sensitivity and rapid response to light and NO_2 gas. These results demonstrate that ZnO thin film transistor can be used for fabricating highly sensitive sensors.

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Curriculum Vitae

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EDUCATION

Johns Hopkins University, USA 2017.09-Present

- Master of Science in Materials Science and Engineering

South China Normal University (SCNU), China 2013.09-2017.06

- Bachelor of Science in Materials Physics

PUBLICATIONS

- **Zhen-xuan Lin**, Bo Huang, Guan-nan He*, Wei-feng Yang, Qin-yu He, Lun-xiong Li, High efficiency enhancement of multi-crystalline silicon solar cells with syringe-shaped ZnO nanorod antireflection layers, ***Thin Solid Films*** 653 (2018) 151-157.
- Guannan He*, Bo Huang, **Zhenxuan Lin***, Weifeng Yang, Qinyu He, Lunxiong Li, Morphology Transition of ZnO Nanorod Arrays Synthesized by a Two-Step Aqueous Solution Method. ***Crystals*** 2018, *8*, 152.

RESEARCH EXPERIENCES

Graduate thesis, Johns Hopkins University 2017.09-Present

Project name: ZnO thin film transistor and its sensor application

- Prepare the ZnO thin film transistor and explore the sensing performance toward different gases and humidity

Undergraduate thesis, SCNU 2016.10-2017.03

Project name: Application of ZnO Nanorod Arrays as Antireflection Layer in Solar Cells

- Prepared the ZnO nanorod arrays by aqueous solution method and obtain different nanostructures including flat-top nanorod, nanocone, syringe-shaped nanorod and cross-link forest by simply adjust the growth conditions
- Applied the as-prepare ZnO nanostructures on multi-crystalline solar cells as antireflection layer and enhanced 47% on the solar cell efficiency

National Natural Science Foundation of China, SCNU 2016.01-2016.10

Project name: Mechanism Research of Charge Transport Properties of Network Transparent Electrode with Quasi-Fractal Structure

- Prepared the quasi-fractal network electrodes and other samples with lift-off lithography process to support the theoretical analysis
- Set up the experimental platform for the preparation of perovskite solar cells including designing the experimental platform and purchasing most of the experimental equipment
- Prepared the compact TiO_2 layer for perovskite solar cell by sol-gel method

China National Undergraduate Innovation Experiment Program, SCNU 2014.03-2016.04

Project name: Bio-template Development of Transparent Conductive Network Electrodes and Their Applications in α-Silicon Solar Cell

- Proposed a novel lithography mask based on the venation of a Magnolia alba leaf
- Prepared the quasi-fractal network electrode on flexible PET substrate by lift-off lithography process with the mask above
- Prepared the α-silicon solar cell with a double n-type layers structure by PECVD attaining an efficiency of 10.97%